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Original Article

EFFECT OF CATALYST ON TRANSESTERIFICATION OF NIGER SEED OIL METHYL ESTER

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ABSTRACT

Various researchers have found a variety of alternative fuels and publicized the use of vegetable oils as alternate fuels for diesel engine. Although, there is a restriction of use of straight vegetable oils as alternate fuels by virtuousness of its high viscosity. In this work, the conversion of methyl ester from neat guizotia abyssinica (Niger) seed oil was undertaken through the transesterification process with four different catalysts. The process was carried out with various operating parameters, such as, methanol to oil molar ratio, catalyst concentration, and the reaction temperature for the conversion of NSOME (Niger seed oil methyl ester). It is observed that, the maximum conversion of NSOME is 99.3% with $KOCH_3$ at a methanol to oil molar ratio of 8:1, catalyst concentration of 1.75%, and at a reaction temperature of 65^oC with 1 hour duration. After the transesterification process the properties of NSOME were tested and assessed to be close to the ASTM standards.

***KEYWORDS:** Niger Seed, Bio- Diesel, Catalyst & Reaction Temperature*

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INTRODUCTION

Biofuels are getting expanded open and scientific awareness, driven by elements such as vulnerabilities related to oil cost, the requirement for the increased energy source, exhaust gas emissions, and assorted variety. Not just the cost of fossil fuels have increased gradually ,in addition, the exhausting of oil, natural gas and coal have increased on account of significant increase in a number of powered vehicles globally [1]. Consequently, production and usage of biodiesel is a better approach to succeed in dealing with problems of vegetable oils. Vegetable oils contain less sulfur and carbon content and thus the biodiesel releases less gaseous emissions than standard diesel [2]. The straight use of vegetable oils in engines results from carbon deposits and choking in the fuel spray nozzle on account of high viscosity and longchain carbon molecules. Therefore, the viscosity of the fuel must be reduced to make fine droplets [3]. Transesterification procedure is the main technique for transforming the large molecular structure into small-scale molecules and the method is economical. Transesterification is the chemical transformation of oil into fatty ester and occurs when the triglycerides mixing with alcohol in presence of catalyst [4]. The catalyst plays an essential role to enhance the reaction rate and yield of methyl ester through transesterification process and $NaOCH_3$ and $KOCH_3$ catalysts in methanol as most favored for large-scale production [5, 6]. The comfortable conversion of methyl esters from high FFA oils is not possible, however, it attempted, it transforms into soaps and thus the decrease of FFA is a vital undertaking [7]. Niger is a year-round herbaceous plant cultivated in India and Ethiopia and the seeds are grown during the spring season in the dry and

warm soil. The rate of seeding changes as 5-8 kg/hectare appears black in color, lightweight and yields 30-40%oil [8, 9]. The physical and chemical properties are comparable with conventional diesel oil and these properties of biodiesel and its blends significantly change with chemical composition, which affects the performance of the engine and exhaust emissions [10, 11]. Eman et al. [12] investigated an experimental study to estimate palm oil methyl ester yield at different operating parameters as such, reaction time, reaction temperatures, and methoxide oil ratios. The optimum yield obtained as 88% at a methoxide oil ratio of 6:1 when the reaction temperature was 60^{o}C with a reaction time of 60 min. Finally, the methyl ester tested for fuel properties which are similar to ASTM standards. Antony *et al*. [13] conducted a test on biodiesel production from Jatropha and its characterization. The consequences of divergent operating conditions like methanol to oil molar ratio, reaction time, the quantity of catalyst and temperature of reaction on biodiesel yield were analyzed. The foremost merger of operating conditions was observed to be 6:1 methanol to oil molar ratio, 60 minutes of reaction time, and 0.92% of the concentration of catalyst and 60^{o}C reaction temperature. Ali *et al.*[14] investigated the production of biodiesel from neem oil and tested for properties. They revealed that the kinematic viscosity of neem biodiesel was 18.1 centistokes lower than the raw neem oil due to transesterification process and found that the density of neem oil was lowered with improved calorific value. Pedro *et al*. [15] studied about the properties of palm oil methyl ester and their blends with diesel as per ASTM standards. The density, higher heating value, cloud point, cetane index, and distillation were found to be matched with ASTM standards. From various literature, the motive of present work deals with the production of methyl ester from neat niger seed oil using four dissimilar catalysts and with a different operating parameter.

MATERIALS AND METHODOLOGY

Collection of Niger Seeds and Extraction of Oil

Basically, the seed is cultivated in India, West Indies, Germany, China, Ethiopia, and Nepal. These seeds contain about 45% of oil and 20% of protein. In this study, the seed was collected from Araku, a hilly region near Visakhapatnam, India, where it is grown in abundance. Prior to the extraction of oil, to remove the moisture, the Niger seeds were dried for 12 hours and at a temperature of 60^{o}C. Then, the oil was recovered from the dried seeds using seed crusher and the quantity of oil was estimated. The obtained oil was degummed, bleached and deodorized before transesterification.

Free Fatty Acid Content in Oil

The FFA substance of oil can be determined using the following procedure. 5 gm of oil was weighed and blended with 30 ml of isopropyl alcohol and 2 or 3 drops of Phenolphthalein pointer was added. This arrangement was titrated with 0.1 N NaOH solutions and the summary in burette is noted. After this collected data, the FFA of oil was calculated as follows.

$$FFA = \frac{282 \times normality of NaOH \times Rundown}{10 \times Weight of oil sample} \tag{1}$$

The FFA of crude Niger seed oil was found to be 4% using the above formula. To reduce this FFA content the following steps are required.

Degumming

A degumming process was carried out to remove the gums present in the raw Niger seed oil. This process may not reduce the FFA but removes the gums, which are not desirable in biodiesel. During this process, 0.1% H_3PO_4 and 0.05% water was added to raw Niger oil and the solution was heated at a temperature of 60°C for 30 minutes. After heating, the

solution was allowed to settle and the settled gums were removed.

Bleaching

As the degumming process is completed, the oil was allowed for bleaching process to remove impurities present in it. Bleaching process was carried out by heating the oil at 90°C and 2% (by weight) of bleaching powder was added to degummed niger oil. Then the temperature was raised to 110°C and allowed to react for 20 minutes. After this process, the bleached oil (i.e. free from impurities) was filtered and collected in a beaker.

Deodorization

FFA reduction of raw oil is an essential factor before preparing biodiesel. Since high FFA cannot be converted into biodiesel easily, when attempted the oil forms soap. Therefore, deodorization process was used to reduce the FFA content of oil. Deodorization is a high temperature, high vacuum steam refining procedure to evacuate unpredictable, odoriferous materials display in the oil. Deodorization process was carried out at a temperature of 240°C - 260°C and a vacuum pressure of 760 torr. Nitrogen gas was used as a carrier gas to carry the free fatty acids. Thereby reducing the FFA content of oil. After the FFA content was reduced the oil was allowed for transesterification process.

Transesterification

The transesterification steps are shown in figures 1 and 2. Transesterification process is the equilibrium chemical reaction of triglyceride and methanol in the presence of a catalyst, giving glycerol and methyl ester (biodiesel). The catalyst enhances the reaction rate and maintains equilibrium.

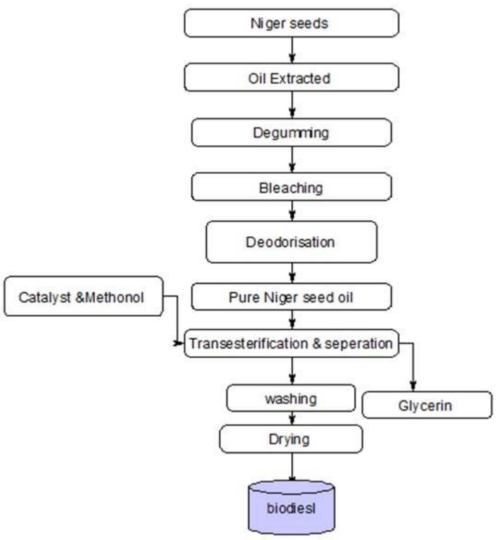

Figure 1: Flow Chart for Preparation of Niger Seed Biodiesel

The transesterification process reduces the viscosity without changing the heating value and cetane number. The following procedure was carried out for producing biodiesel. In this study, four different (i.e. $KOCH_3$, $NaOCH_3$, KOH and NaOH) alkaline catalysts were used to improve the rate of reaction and different operating parameters (i.e. methanol to oil molar ratio, the concentration of catalyst, reaction temperature and the reaction time). 100 grams of raw Niger seed oil was taken into a 500 mL round flask and heated at a temperature of 65^{o}C. The heated oil was added with a methanol-catalyst solution and allowed for stirring during one hour.

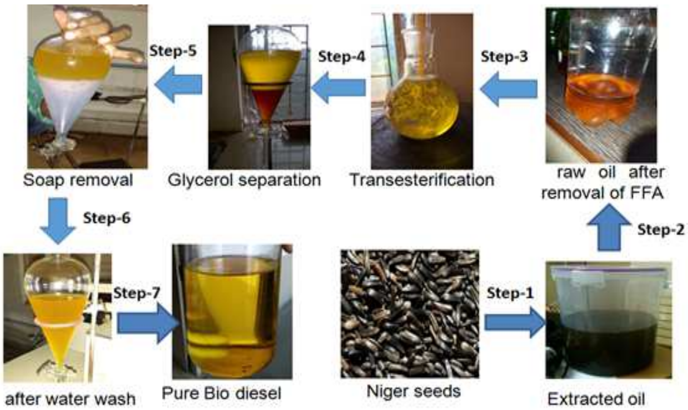

Figure 2: Preparation of Niger Seed Biodiesel

After the transesterification process, the glycerol was separated in separating flask and the obtained methyl ester was allowed for water wash to remove the soaps present in it. At the end, the biodiesel was allowed for heating to remove water particles present in the biodiesel. The yield of biodiesel was estimated and recorded. The above procedures were repeated by varying the operating conditions and catalysts. The optimum value was noted and produced a large quantity of biodiesel for testing of properties and investigations on diesel engine.

PROPERTIES OF BIODIESEL

After the transesterification process, the physio-chemical properties of biodiesel were assessed and compared with standard diesel oil. The following properties were evaluated as per ASTM standards. Relative density, kinematic viscosity, acid value, cetane number, high heating value, flash point, cloud point and copper corrosion value. These properties were estimated for different catalysts and presented in the following table1.

Table1: Properties of Niger Seed Methyl Ester

Fuel Property	Method	ASTM Value	NSOME Property Values with Different Catalysts			
			Na OH	KOH	$NaOCH_3$	$KOCH_3$
Acid Number (mg KOH/g), %	ADTM D6571	0.8 (maximum)	0.3	0.3	0.3	0.3
Relative Density at 15°C (kg/m^3)	ASTM D-1298	860-900	884.6	882.7	888.7	889.4
Kinematic Viscosity at 40°C (Cts)	ASTM D-445	2.5-6	4.362	4.17	4.113	3.964
Heatingvalue (MJ/kg)	ASTM D -4809	42	41.08	41.11	41.25	41.86
Cetane Number	ASTM D-976	47 (minimum)	59	59	60	60
Copper Corrosion test	ASTM D-130	1 (maximum)	1b	1a	1a	1a
Cloud point (^oC)	ASTM-97	6 (maximum)	3	3	3	3
Flashpoint (^oC)	ASTM D-92	130 (minimum)	169	169	169.	170

RESULTS AND DISCUSSIONS

Influence of Various Operating Parameters of Transesterification on the NSOME Yield

The yield of biodiesel was found to be depending on the type of catalyst used and other key parameters of reaction viz., the solvent to seed oil ratio, the concentration of catalyst. The details of parametric trends are given in the following paragraphs.

Effect of Methanol to Oil Molar Ratio

The variation of NSOME conversions of various catalysts is shown in figure.3. Methanol to oil molar ratio is an essential variable which effects the conversion of methyl ester yield. This mainly depends on the type of oil used, since it ends up with a large amount of unreacted material, which results in slow reaction rate.

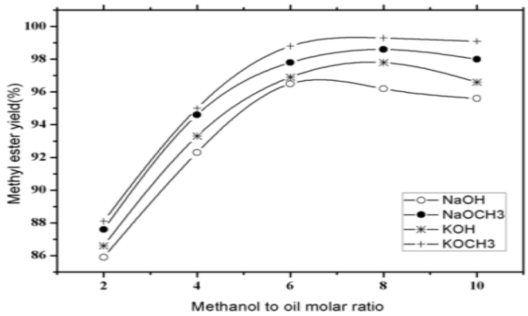

Figure 3: Effect of Methanol to Oil Molar Ratio on Bio Diesel Yield

When the methanol to oil molar ratio is greater than the stoichiometric ratio, the higher conversions of methyl ester are possible in a short time period, since a large amount of alcohol is used for conversion of triglyceride to methyl esters. Experiments were carried out at molar ratios from 2: 1 to 10:1, reaction temperature of 65°C and catalyst concentration of 1.75 %. The highest conversion of NSOME 99.3% was found at 8:1 molar ratio of $KOCH_3$. $KOCH_3$ gave better NSOME conversion than other catalysts. It was also observed that the NSOME yield was reduced with a further increase in molar ratio, since the glycerin separation was complicated due to increase in solubility.

Effect of Concentration of Catalyst

Because of emulsification, glycerin separation reduces, which results in a decrease of ester conversion of bio-diesel. Observations from the present study reveal that, the conversion of NSOME decreased with further increase in catalyst concentration from the optimum value. Also, with insufficient concentrations, it is not possible to convert the bio-diesel through transesterification. In this study, the ester conversion was carried out with different catalysts like $KOCH_3$, $NaOCH_3$, KOH and NaOH. All the reactions were carried at fixed methanol to oil molar ratio of 8:1 and a reaction temperature of 65^{o}C for an hour. Highest conversion of NSOMEwas found at 1.75 % of $KOCH_3$with 99.3% yield, 1.75 % of $NaOCH_3$ with 98.6% yield, 1.5 % of KOH with 97.8 %, and at 1.25 % of NaOH with 96.2% of yield. the variation of NSOME conversion is shown in figure.4.

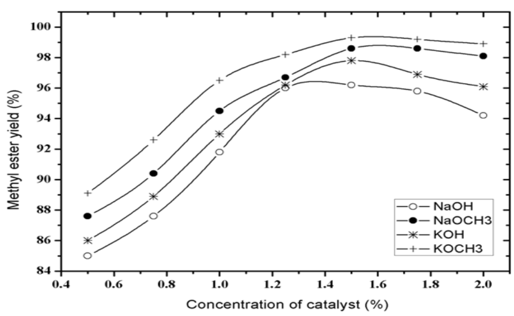

Figure 4: Effect of Concentration of Catalyst on Biodiesel Yield

Effect of Reaction Temperature

The reaction rate was mainly influenced by the temperature, because of reaction rate increases with an increase in temperature. Therefore, the ester conversion at lower temperatures could not be completed. However, at higher reaction temperatures the ester conversion decreases. Based on critical observation, emulsification of glycerine and an excessive loss of methanol, the reaction could be completed even at room temperature with $KOCH_3$ and $NaOCH_3$as catalysts. In this study, the highest yield of NSOME was obtained with a reaction temperature of 65°C and at a fixed methanol to oil molar ratio (8:1), the concentration of the catalyst (1.75%).

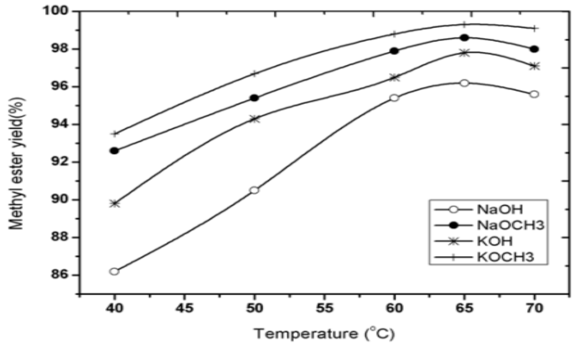

Figure 5: Effect of Reaction Temperature on Biodiesel Yield

Temperature variation of ester conversion of NSOME is presented in Figure 5. It is also observed that, there is a decrease in NSOME conversion after 65°C.

CONCLUSIONS

- A comparison of the effect of different catalysts used in the production of NSOME was carried out and it is found that potassium methoxide followed by sodium methoxide gave good results in terms of yield and properties. It is also observed that, triglycerides could be fully transesterified within 3 to 5 minutes even at room temperatures.
- It was found that, a yield of 99.3% NSOME with $KOCH_3$ as acatalyst at an optimum methanol to oil ratio of 8:1 with 1.75% of catalyst concentration, a reaction temperature of 65°C and reaction duration of 1 hour.
- The properties of biodiesel obtained from niger seeds were as per desirable requirements of ASTM standards. There is an improvement in certainc number which would results in better combustion of fuel in the engine. There was no deterioration in the corrosivity of the biodiesel and same as normal petrodiesel.

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